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STRUCTURAL INVESTIGATION OF Li_2O-B_2O –Al_2O_3 GLASSES BY XRD, DTA AND DENSITY MEASUREMENT

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ABSTRACT

Glasses of the 30 Li_2O – (70 – x) B_2O_3 - x Al_2O_3 system (where x = 0, 5, 10, 15, 20) were prepared by melt quenching technique and investigated by XRD, DTA and density measurement. The XRD analysis of prepared sample confirms the nature of sample. The density and molar volume studies reported the change of structure with the increases of aluminum content. The DTA measured glass transition temperature (T_g) of samples, glass forming ability (GFA) and glass stability (GS).

KEYWORDS: XRD, Density, Molar Volume, DTA

INTRODUCTION

B_2O_3 is one of the most important glass forming oxides and has been incorporated into variation kinds of glass systems in order to attain the desired physical and chemical properties. Since the past several years, borate glasses have attracted much attention because of their electrochemical and optical application namely as solid state batteries, optical waveguide and luminescent material. Several previous works on borate glasses are devoted to studying the structures, magnetic and electrical properties [1–5]. The properties of borate glasses are commonly attributed to the fact that boron atom can assume trigonal and tetrahedral coordination and also to different ways through which the borate building can be linked together [6]. The concentration of various borate species in the glass structure is determined by nature and concentration of modifier oxides. Oxide glass containing Li^+ ions is one of promising candidate for electrolyte material of thin film batteries because it exhibits an isotropic ionic conduction and stability at high voltage [7]. Lithium borophosphate glasses have been studied extensively in literature [8-10] because of interesting structure and physical property changes upon network modification. These systems contain two different glass formers (B & P) in the glass network responsible for changing the structure. The changes in structure due to replacement of one former cation (P) by other one (B) and formation of various and phosphate structural unit in the glass network, if the total ion concentration is kept constant. The observed behavior is usually called “Mixed glass former effect”. Several workers [11-17] have been proposed to reflect relative glass forming ability (GFA) and glass stability (GS) on the basis characteristic temperature measured by Differential scanning calorimetric (DSC) and differential analysis (DTA). In the present work, we reported a structural characterization of Lithium aluminoborate glasses by mixed glass former effect.

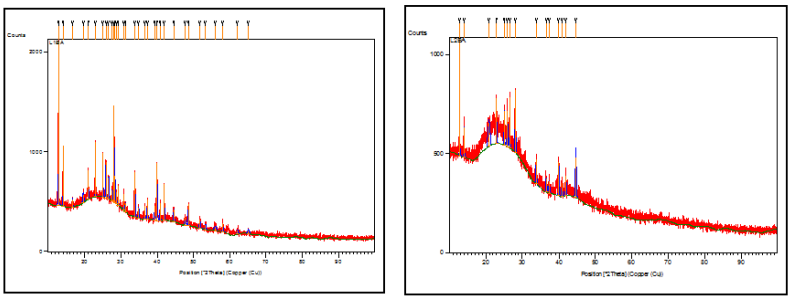
EXPERIMENTAL

The lithium borate glasses of the composition 30 Li_2O – (70 – x)B_2O_3 - x Al_2O_3 (x = 0, 5, 10, 15, 20) were prepared by melt quenching method technique. The starting material Li_2CO_3, $B(OH)_3$ and Al_2O_3 of AR grade purchased

from Merc Laboratory were used. The homogeneous mixture has melted in ceramic crucible in Muffle Furnace (Biotech India) equipped with digital temperature controller. The sample were melted at 1150^0c for two hours with the heating rate 30^0c/min. the molted material were stirred several times to ensure a complete homogeneity of the samples, then they were quenched in Aluminum mould at room temperature. The samples were annealed at 200^0c for 2Hrs in hot air oven. The XRD of prepared sample were examined by using XPERT PRO diffractometer. Differential thermal analysis measurements were carried using NEFZ SCH STA 449F1 instrument in the temperature range from 323K to 773K (using Al_2O_3 powder as reference material) Glass density was measured at room temperature using standard Archimedes method with Benzene as immersion fluid of density (0.886gm/cm^3). The experimental error was about ± 0.003 gm/cm^3. The molar volume (V_m) was calculated from molecular weight and density (ρ).

RESULTS AND DISCUSSIONS

All the results are presented as a function of x mole percent Al_2O_3 treating the investigated sample as 30 Li_2O: (70 – x) B_2O_3: x Al_2O_3 (x = 0, 5, 10, 15, 20). Figure 1 shows the XRD pattern of investigated glass samples. The peak is observed for glass samples, indicates that these glass samples are composed of glassy phase. However some glasses sample shows sharp diffraction peak super imposed on weak halo pattern, indicating partial crystallization occurred. Therefore the glass samples are composed of glossy phase and partially crystalline phases. The result of XRD shows that these samples are still amorphous. It is observed that the glassy phase in sample increases with mole percent of Al_2O_3 or decreasing with increases of former ratio.



(a) (b)

Figure 1: XRD of Glass Samples (a) L1BA Sample (b) L2BA Sample

Figure 2 shows the DTA curve of glass samples free from Al_2O_3 and sample containing Al_2O_3 up to 20 mole percent. The effect of percentage of Al_2O_3 in on thermal transition data for investigated samples L_1BA-L_5BA is shown in figure 3. The values obtained from DTA graph is depicted in the Table 1. In the interpretation T_g, T_x, and T_1 are glass transition, Onset melting temperature and offset melting temperature respectively. It is observed that from Figure 3 (a & b) that glass transition temperature are shifted to higher temperature with increasing mole percentage of Al_2O_3 and decreases with increasing former ratio. One exothermic peak follows the glass transition temperature indicating the first crystallization process. The exothermic peak followed by two endothermic for first four samples, which show that the melting process take place in two steps, while fifth sample have one endothermic peak, Tm (on set melting temperature). It shows that Tx increases with increasing mole percentage of Al_2O_3. Higher value of Tx is the higher thermal stability of amorphous [11]. The offset melting temperatures (T_1) are shifted to higher temperatures by increasing percentage of Al_2O_3.

The substitution of former Al_2O_3 in Li_2O:B_2O_3 for the glass causes the change in value of T_g, T_x and T_1 of the samples. This effect depends on 1) density of covalent cross linkage, 2) oxygen density of the network and 3) number and strength of the cross links between oxygen and cations. In this case the values of Tg are higher than that of samples free from Al_2O_3. The introduction of substitution Al_2O_3 changes the former ratio since in this case modifier ratio is kept constant. Some of covalent B-O Bonds in the glass network to be replace by Al-O bonds. This causes a increase in bond strength and also increase in T_g values of sample [12]. The increase in T_g value reveals that the structure of glass sample is modified. It could be assumed that in this case Al_2O_3. Can be incorporated into network resulting in the formation of B-O-Al linkages with covalent character, which yields a mixed network forming character in accordance with increase in T_g.

There are several parameters have been used to estimate Glass forming ability (GFA) of glasses.

- The reduced glass transition temperature $T_{rg}=T_g/T_1$ which reflects the difficult of nucleation of crystallization phase during cooling from super-cooled liquid **[13-16]**. The reduced glass transition temperature Trg has higher value at 5 mole percent of Al_2O_3 content glass sample indicates GFA and high thermal stability of the super cooled liquid region against crystallization. The value of ΔT_x, defined as $T_x - T_g$, is large for 5 mole percent of Al_2O_3. Content glass sample, it shows that super-cooled liquid can exist in wide temperature range without crystallization and leading to good GFA [17]. The comparatively values of ΔT_x of other samples reveal that there are not fully glassy state and also not in fully crystalline state.

- The reduced crystallization temperature $\gamma=T_x/T_g+T_1$ shows stronger correlation with GFA and T_{rg}. The value of γ is large for 5 mole percent of Al_2O_3 content glass sample, indicate high GFA and greater thermal stability **[11].** Hruby proposed that parameter K_H obtained by DSC or DTA indicates glass stability against crystallization on heating [17, 18]. This parameter is defined as $K_H = (Tx-Tg)/(T_1-Tx)$ the large value of greater stability of glass against devitrification. The value of K_H is large for L2BA glass sample hence this sample is more stable against crystallization.

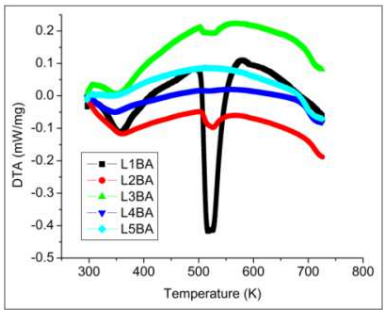


Figure 2: DTA Curve of Samples

Table 1: The Values Obtained from TG DTA Graph for L1BA-L5BA Series

Sample	Mole% Al_2O_3	Former Ratio(Y)	Tg (K)	Tx (K)	Tp (K)	T1 (K)	Trg	ΔTx(K)	γ	K_H
L1BA	0	1	500	520	580	614	0.814332	20	0.466786	0.2127
L2BA	5	0.9285	503	525	565	600	0.838333	22	0.475975	0.2933
L3BA	10	0.8571	508	525	561	650	0.781538	17	0.453368	0.1360
L4BA	15	0.7857	512	532	560	710	0.721127	20	0.435352	0.1123
L5BA	20	0.7142	550	565	520	700	0.785714	15	0.467715	0.1111

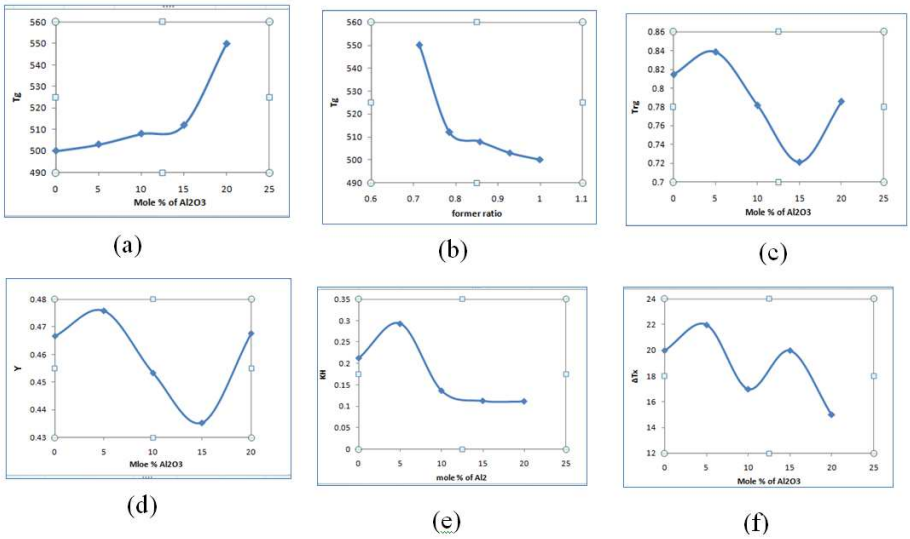


Figure 3: Effect of Al_2O_3 Content on Thermal Transition Data for Investigated Samples (a) Tg vs Al_2O_3 Content (b) Tg vs Former Ratio (c) Trg vs Al_2O_3 Content (d) ϒ vs Al_2O_3 Content (e) K_H vs Al_2O_3 Content (f) ΔTx vs Al_2O_3 Content

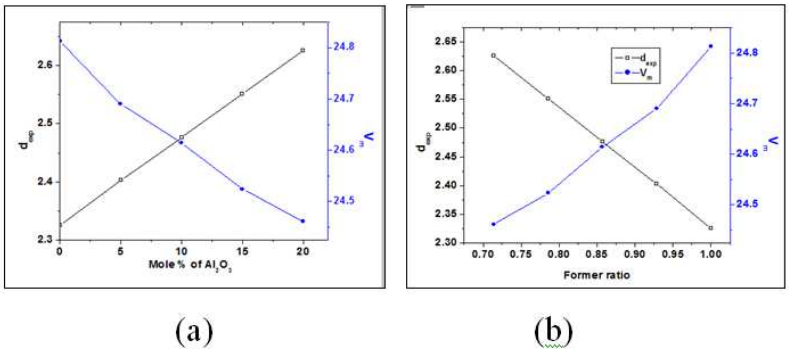


Figure 4: Variation of Molar Volume and Density of Glass (a) with Mole % of Al_2O (b) with Former Ratio

The density measurement is very sensitive tool that can easily detect any changes in the glass network. The variation of density and molar volume with mole percent of Al_2O_3 is depicted in Figure 4. It is observed that density of glass increases while molar volume decreases with increase of mole percent of Al_2O_3. So the increase in density of investigated glass samples could be attributed to be difference in properties of both lithium oxide and aluminium oxide. Most of aluminium enters as modifier in glass samples network and also non – bridging oxygen decreases in the glasses network by increasing aluminium oxide which consolidate their structure and increase the density [19]. However according to Shelby [20] the presence of Al_2O_3 in glass causes BO_3 coordination by using oxygen available from Li_2O, which is required to convert BO_3 to BO_4, therefore the net result is to shift coordination (BO_3) to (BO_4) and hence increase in density. Then observed result well agree with the literature also [21].

The glass molar volume Vm was calculated, it decreases with increasing Al_2O_3 content as shown in the steepest change in molar volume. Occurs at the concentration above 15 moles per. This could be explained by considering B –O – B linkage [22] with strong covalent bond B and Al oxygen bond. Thus substitution of longer Li – O bond for shorter covalent bond leads to close structure of glasses. Investigation of all samples shows that introduction of Al_2O_3 caused an increase in Tg and decrease in the molar volume

CONCLUSIONS

According to the obtained results, it concluded that the XRD Pattern of the investigated glass samples are composed of glassy phase and partially crystalline phase. GFA parameters ΔT_x and γ follow the same trend with GS parameters K_H. The increase in mole percent of Al_2O_3 affects on an increase in glass transition temperature T_g, increase in density and decrease in molar volume. The increase in density is attributed to closing up of glass structure due to change from BO_3 to BO_4 group. The BO_3 and BO_4 group act as network structural group while Lithium and Aluminium appear in interstitial position.

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REFERENCES

1. E. I. Kamitos, G.D. Chryssikos, J. Mol. Struct.247 (1991) 1
2. E. I. Kamitos, M. A. Karakassides, Phys. Chem. Glasses 30 (1989) 229.
3. C. P. Varsamis, E. I. Kamitos, G.D. Chryssikos, solid state ionics 136 (2000) 1031.
4. D. Mainu, T. Illiescu, I. Ardelean, J. S. Cinta Pinzaru, N. Tarcea W. Kiefer, J. Mol. Struct. 485 (2003) 651–653.
5. R. Ciceo lucacel, I Ardelean, J. Optoelectron. Adv. Mater. 8 (2006) 1124.
6. D. L. Griscomk, Material science Research on Bortate Glasses, Ed. By L. D. Pye, V. D. Frechette and N. J. Kredl, Plenum press, New York (1978)
7. Young I. I. Lee, Jong – Heun Lee, Seong _ Hyeon Hong, Youngsin Park, Solid State Ionics 175 (2004) 687.
8. A. Magnistric, G. Chiodelli, M. Villia J. Power Sources 14 (1985) 87–91.
9. B. K. Money, K. Hariharan, Solid State ionics 179 (2008) 1273–77.
10. F. Munoz, L. Montagne, L. Pascial, A. Duran J. Non. Cryst. Solids 355 (2009) 2571 – 2577.
11. Z. P. Lu & C. T. Lu, Acta Mater 50, (2002)3501.
12. A.A. Soliman, Egypt J. Solids 21, (1998)2
13. Z. P. Lu, H. Li & S. Ng, J. Non crystal. Solid 270(2000)103
14. M. Shapaan, A Bardos, L. K. Varga & J. Lendvai, Central European Journal of phys. 2(2004)104
15. M. Shapaan, A Bardos, L. K. Varga & J. Lendvai, Mater Sci. Eng. A366 (2004) 6
16. A. Inoue, Y. Yokoyama, Y. Shinohara, T. Masumoto, Mater. Trans. JIM, 35(1994)923
17. I. Avramov, E. D. Zanotto & M. O. Prado, J. non crystalline Solid, 320,(2003)98
18. A. Hruby, Czech. J. Phy. B22, (1972)1187
19. T. Abe “Journal of Amesical Ceram Societ,” 35 (1952) 11

20. J. E Shelby, Introduction to glass science and technology (the Roya Society of Chemistry, Cambridge, U.K. 1997)

21. M. Sibata, C. Sanchez, H. palel, S. feller, J. Stark, G. S, and J. Sumcad, and J. Kaspar, J. Crystalline Solids 85,(1986) 29

22. M. Ganguli & K. J. Rao “Journal Solid State Chem.” 145 (1999) 65